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Technical Report No. 6

Molecular Dynamics of Macrocycle-Metal Ion Complexes
Involving Heteronuclear Binding Atoms

by

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Prepared for Publication

in

Pure and Applied Chemistry

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January 23, 1989

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited.	
2b DECLASSIFICATION / DOWNGRADING SCHEDULE				
4 PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 6			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION University of Utah	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION		
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Utah Salt Lake City, UT 84112		7b ADDRESS (City, State, and ZIP Code)		
8a NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0639		
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		10 SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO	PROJECT NO	TASK NO
		WORK UNIT ACCESSION NO		
11 TITLE (Include Security Classification) (U) Molecular Dynamics of Macrocyclcye-Metal Ion Complexes Involving Heteronuclear Binding Atoms				
12 PERSONAL AUTHOR(S) Licesio J. Rodriguez, Meizhen Xu, Edward M. Eyring* and Sergio Petrucci				
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/87 TO 1/89	14. DATE OF REPORT (Year, Month, Day) 1989, January 23		15. PAGE COUNT 4
16. SUPPLEMENTARY NOTATION Prepared for publication in Pure and Applied Chemistry				
17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			ultrasonic absorption, nonaqueous solutions, Krptofix 22, crown ethers. (mgm) ←	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Edward M. Eyring			22b TELEPHONE (Include Area Code) (801) 581-8658	22c OFFICE SYMBOL

MOLECULAR DYNAMICS OF MACROCYCLE-METAL ION
COMPLEXES INVOLVING HETERONUCLEAR BINDING ATOMS

Licesio J. Rodriguez, Meizhen Xu, Edward M. Eyring and
Sergio Petrucci

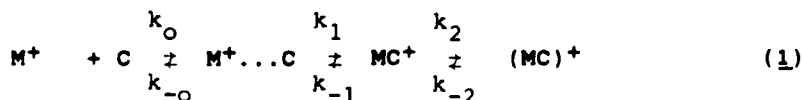
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Abstract - Combination of ultrasonic absorption relaxation spectra with infrared absorption spectra yields a clearer picture of the mechanism of complexation of metal ions by macrocycles in nonaqueous solutions. The Eigen-Winkler multistep reaction mechanism has consistently provided a suitable fit of the ultrasonic absorption data for systems such as monovalent sodium cation reacting with 18-crown-6 in acetonitrile. A macrocycle such as Kryptofix 22 having two nitrogen atoms in the ring experiences an exo-exo \rightleftharpoons exo-endo \rightleftharpoons endo-endo change in conformation readily detected by ultrasonic techniques. Differences in complexation-decomplexation mechanisms deduced from ultrasonic and NMR data can be rationalized in terms of the limitations of the experimental techniques.

INTRODUCTION

Ultrasonic absorption data in the frequency range between 0.5 and 500 MHz can be collected by a judicious combination of ultrasonic resonators, laser Debye-Sears diffraction experiments and ultrasonic pulse methods (ref. 1). Early examples of the use of ultrasonic methods to study rates and mechanisms of reactions of macrocycles include a classic study of sodium cation complexation by valinomycin in methanol (ref. 2) and several papers describing monovalent and divalent cations undergoing complexation by 18-crown-6 and 15-crown-5 in aqueous solutions (ref. 3). In recent years we have shifted our attention to kinetic studies of macrocycles reacting with cations in aprotic solvents (ref. 4). To some extent this new interest has been driven by practical considerations such as the exploration of reaction rates in lithium battery electrolytes (ref. 5).

The Eigen-Winkler multistep reaction mechanism (ref. 6) may be written as



Here M^+ denotes the metal ion, C the macrocycle, $M^+ \cdots C$ a solvent separated pair, MC^+ a contact pair of solutes, and $(MC)^+$ the metal ion imbedded in the cavity of the macrocycle. Scheme 1 is necessarily a considerable oversimplification since each of the species can exist in more than one configuration (ref. 6). In the first step (on the left) an outer-sphere complex forms requiring some change in the conformation of the ligand C and partial desolvation of the cation. The third step (proceeding from left to right) can be rate limiting either by desolvation (as in water) or by ligand rearrangement. The relatively high permittivity of aqueous solutions favors high concentrations of the free metal ions. The competition of solvent water molecules with counteranions and macrocyclic ligands for positions in the first coordination sphere of the metal ion is tilted heavily in favor of the solvent water. The familiar generalization (ref. 7) for aqueous solutions that the rate limiting step in metal-ligand complex formation is the loss of a solvent water molecule from the first coordination sphere of the metal ion arises from this unequal competition between solvent, counteranion, and ligand suitors.

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$$\text{LiAsF}_6 + \underset{k-1}{\overset{k_1}{\rightleftharpoons}} \text{LiAsF}_6 \dots \underset{k-2}{\overset{k_2}{\rightleftharpoons}} \text{LiCAsF}_6 \quad (2)$$

RECENT DEVELOPMENTS

The figure shows four diagrams of a hexagonal molecule, labeled 1 through 4, representing different substituent patterns at the 1, 3, and 5 positions:

- 1:** A hexagon with a small circle at each of the 1, 3, and 5 positions.
- 2:** A hexagon with a small circle at each of the 1, 3, and 5 positions. The top vertex (position 2) is labeled 'N'.
- 3:** A hexagon with a small circle at each of the 1, 3, and 5 positions. The top vertex (position 2) is labeled 'N', and the bottom vertex (position 4) is labeled 'N'.
- 4:** A hexagon with a small circle at each of the 1, 3, and 5 positions. The top vertex (position 2) is labeled 'N' and has a wavy line extending upwards. The bottom vertex (position 4) is labeled 'N' and has a wavy line extending downwards.

$$\text{endo-endo} \pm \text{endo-exo} \pm \text{exo-exo} \quad (3)$$

It must then be assumed that the protic solvents give rise to a more even distribution of the cryptand 3 among the three species thus facilitating the detection of two ultrasonic relaxation processes. Two ultrasonic relaxation processes are detected for Kryptofix 22 2 in both acetonitrile and methanol that are also accounted for by eq. 3. Judging from differences in the ultrasonic spectra of the diaza crowns 2 and 4 in methanol, the long alkyl chains of 4 slow considerably the rotation of the

nitrogen atoms in 4 compared to those in 2.

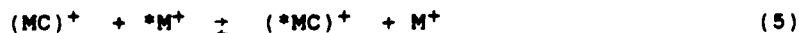
Infrared spectral data can enhance our understanding of conformational changes of macrocycles in solution like those described above. For instance, spectra in the $\sim 800\text{--}900\text{ cm}^{-1}$ region for 18-crown-6 dissolved in acetonitrile show three bands at 857, 842.5 and 835 cm^{-1} that are dominated by the comparatively large 842.5 cm^{-1} peak (ref. 14). Predominance of one configuration of the macrocycle is consistent with the observation in acetonitrile of only one ultrasonic relaxation arising from an equilibrium between the dominant form and one of the other two configurations. Infrared spectral data obtained from $\sim 0.1\text{ M}$ concentrations of NaClO_4 and NaSCN dissolved in acetonitrile also show that contact ion pairs are present in this comparatively low donor number ($\text{DN} = 14.1$) solvent (ref. 14). However, ultrasonic absorption data for sodium perchlorate, sodium tetraphenylborate and sodium thiocyanate dissolved with 18-crown-6 in acetonitrile are quite similar indicating that the sodium cation-crown ether interaction is stronger than the cation-anion interaction even in this low donor number solvent (ref. 14). These are good examples of the valuable synergism that arises from applying both ultrasonic and infrared spectral techniques to a given dissolved macrocyclic system.

Stopped-flow techniques had been used successfully for a long time to study the comparatively slow complexation of metal ions by cryptands (ref. 15). Hence we were pleased and a little surprised at first by the rich complexity of the ultrasonic absorption spectra of alkali metal cations dissolved with 222 cryptand in dry propylene carbonate (ref. 4). It turns out that one is able to observe two relaxation processes corresponding to first-order or pseudo-first-order rate processes. They are attributed to a process like that shown in eq. 3 wherein the cryptate undergoes successive intramolecular rearrangements, probably involving nitrogen rotation, with the coordinated metal ion never detaching from the macrocycle. When the diaza compound 2 reacts with silver cation in acetonitrile the ultrasonic absorption results are similar to those obtained for silver cation and compound 3 in the same solvent (ref. 16). Evidently, the presence and geometrical positioning of the nitrogen atoms of the two ligands, rather than the presence or absence of a third ethereal chain, are the key factors in the dynamics that are detected by ultrasonic absorption. Many additional details of the mechanism of complexation of metal ions by macrocycles could be distilled from recently published ultrasonic absorption studies.

Nuclear magnetic resonance data (ref. 17) indicate that for solutions in solvents of low donor number such as acetonitrile and nitromethane ($\text{DN} = 2.7$) dissociation of a metal-macrocycle complex is not initiated by the solvent molecule S as in eq. 4



and as we have inferred from the ultrasonic absorption experiments described above. Instead NMR data (ref. 17) are consistent with the initiation of dissociation by metal cations in excess as in the following exchange reaction



Mechanism 5 is particularly important for large crown ethers such as dibenzo-24-crown-8 and dibenzo-30-crown-10. For instance, Shamsipur and Popov (ref. 18) used cesium-133 NMR to study the interaction of the cesium cation with dibenzo-30-crown-10 in nitromethane, acetonitrile, propylene carbonate and methanol. At temperatures below 263 K the exchange mechanism of eq. 5 dominates in the last three solvents. From thermodynamic data on crown ether complexation of metal ions in nonaqueous solvents (ref. 19) it is evident that the stability constant for a metal ion-crown ether complex increases as the temperature decreases. Thus as temperature decreases there is less affinity between the solvent S and the $(\text{MC})^+$ complex necessary to initiate reaction 4. If another potential attacker of $(\text{MC})^+$ is present such as M^+ in excess (or anion X^- in excess), reaction 5 or its analogue reaction 6



could become important.

Ultrasonic absorption techniques cannot detect a process such as reaction 5 since the molar volumes and molar enthalpies are unchanged as reactants proceed to products. In non-aqueous media of low permittivity ultrasonics even fail to detect the initial second order step of reaction 1 because the stability constant is so large. What ultrasonic methods detect instead are the intramolecular changes of $M^+ \dots C$, MC^+ and $(MC)^+$ under the influence of an adiabatic pressure wave. The NMR method also fails to detect the initial second order step of reaction 1 because the forward process is too fast; it can only detect the initial attack of the reverse process of reaction 1 or, if you like, the initial attack of reactions 4, 5 and 6. Because of these inherent differences in the two methods and particularly because of the difference in their accessible time scales it is not certain that the results obtained by these two methods on a system such as cesium cation plus dibenzo-30-crown-10 in acetonitrile at low temperatures can be checked against one another very effectively. However, the experiments certainly should be carried out.

Acknowledgements. The organizers of the conference are thanked for their invitation. This research received generous financial support from the National Science Foundation (Grant No. CHE85-13266) and a grant from the Office of Naval Research.

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